

1                   **MULTIPLE HYDROPROCESSING REACTORS**  
2                   **WITH INTERMEDIATE FLASH ZONES**

3  
4                   FIELD OF THE INVENTION

5  
6       This invention relates to hydrocracking, and more particularly to second stage  
7       hydrocracking employing multiple reaction zones.

8  
9                   BACKGROUND OF THE INVENTION

10  
11      Fuel demands are increasing worldwide. The fuels produced must meet  
12      stringent standards concerned with environmental quality. The most abundant  
13      feedstocks currently available are relatively heavy, such as vacuum gas oil and  
14      Fischer-Tropsch streams. Hydrocracking is used to convert heavy hydrocarbon  
15      feedstocks into lighter materials which may be used to make middle distillate  
16      products.

17  
18      Hydrocracking is typically performed in one or more staged hydrocracking units  
19      that can be independent reactors or combined into multi-staged reactors. All  
20      hydrocracking processes aim to maximize yield and minimize recycle volume. In  
21      most cases, however, yield maximization results in increased recycle, and vice  
22      versa.

23  
24      U.S. Pat. No. 5,705,052 discloses a process for hydroprocessing liquid petroleum  
25      and chemical streams in a single reaction vessel containing two or more  
26      hydroprocessing reaction stages. Both feedstock and treat gas flow co-currently  
27      in the reaction vessel. The whole partially converted hydrocarbon effluent  
28      passes to the next reaction zone after being stripped of its "dissolved gaseous  
29      material".  
30

1 U.S. Pat. Nos. 5,720,872 and 6,103,104 are variations of the process described  
2 in U.S. Pat. No. 5,705,052. In U.S. Pat. No. 5,720,872, the major difference is  
3 the addition of a multi-staged stripper in a single stripper vessel. U.S. Pat.  
4 No. 6,103,104 employs the concept of interbed quench between the  
5 hydroprocessing stages.

6  
7 U.S. Pat. No. 6,017,443 discloses a process for catalytic hydroprocessing, in  
8 which a feedstock is introduced at the top of the lower reaction zone for  
9 downward flow through and reaction with the catalyst therein. In one  
10 embodiment, a partially reacted liquid effluent is pumped from the lower reaction  
11 zone to the top of the upper reaction zone for downward flow through and  
12 reaction with the catalyst in that zone. The recycle is not fractionated into  
13 product and unconverted material prior to recycling, however.

14  
15 U.S. Pat. No. 4,082,647 discloses a hydrocracking process with two reactors  
16 operating in parallel rather than in series. Two different feedstocks may be  
17 hydrocracked to maximize distillate production. The second feed is mixed with  
18 the vaporous phase from separation of effluent from the conversion of the first  
19 feedstock.

20  
21 U.S. Pat. No. 4,197,184 discloses a conventional multiple-stage process for  
22 hydrotreating and hydrocracking a heavy hydrocarbonaceous charge stock. In  
23 the process, hydrocracked effluent is admixed with hydrotreated effluent and the  
24 combination separated into a hydrogen rich vaporous stream and normally liquid  
25 material. The cooled vapor stream is then used as a source of hydrogen and as  
26 a quench fluid for both the hydrotreating reaction zone and the hydrocracking  
27 reaction zone.

28  
29 U.S. Pat. No. 6,106,695 discloses a process having more than one  
30 hydrocracking reaction zone which contains hydrocracking catalyst, wherein the  
31 catalyst is rejuvenated or reactivated while the process unit remains on-stream

1 by the periodic exposure of partially spent catalyst to hot recycle gas containing  
2 hydrogen. The reactors in this process operate in parallel rather than in series.

### 4 SUMMARY OF THE INVENTION

6 The instant invention comprises a hydroprocessing method having at least two  
7 stages. The first stage employs a hydroprocessing catalyst which may contain  
8 hydrotreating catalyst, hydrocracking catalyst, or a combination of both. The  
9 second stage employs a series of fixed bed reaction zones, with feed and  
10 hydrogen in co-current flow, with inter-bed removal of gas and products. Gas  
11 and product removal occur in a flash separation zone in which hydrogen  
12 preferably enters countercurrently.

14 The process of the instant invention maximizes middle distillate yield while  
15 minimizing the volume of recycle. Per-pass conversion is defined as fresh feed  
16 converted in a stage divided by total feed to a stage. The per-pass conversion  
17 rate in each reactor vessel remains low, 40% or less, while the overall conversion  
18 rate is 60% or greater.

20 The process of this invention provides economy in equipment employed. Single  
21 bed reactors, which are smaller, have lower capacity, and are easier to maintain  
22 than multiple bed reactors, may be used. The use of small, single bed reactors  
23 provides flexibility in second stage operation. They are of simple design and do  
24 not require quench gases or liquids. This promotes economic operation.

26 The hydroprocessing method of the instant invention, which has at least two  
27 reaction stages, comprises the following steps:

- 29 (a) passing a hydrocarbon feed into a first reaction stage, which is maintained  
30 at hydroprocessing conditions, where it is contacted with a catalyst in a  
31 fixed bed and at least a portion of the feed is converted;

- 1 (b) combining the effluent of step (a) with product material from the second  
2 reactor stage and passing the combined stream to a separation zone;  
3
- 4 (c) separating the stream of step (b) into an unconverted liquid effluent and at  
5 least one converted stream comprising products having a boiling point  
6 below that of the feed;  
7
- 8 (d) passing the unconverted liquid effluent from step (c) to a second reaction  
9 stage, said stage comprising a plurality of reaction zones, wherein each  
10 zone is maintained at hydrocracking conditions and separation occurs  
11 between each zone;  
12
- 13 (e) contacting the feed in the first reaction zone of step (d) with a catalyst in a  
14 fixed bed, thereby converting at least a portion of the feed;  
15
- 16 (f) separating the effluent of step (e) into an unconverted liquid effluent, and a  
17 hydrogen-rich converted stream;  
18
- 19 (g) recycling the hydrogen-rich converted stream of step (f) to combine with the  
20 effluent of step (a);
- 21 (h) passing the unconverted liquid effluent from step (f) to a second reaction  
22 zone of the second stage, the zone being maintained at hydrocracking  
23 conditions;  
24
- 25 (i) contacting the feed in the second reaction zone of step (h) with a catalyst in  
26 a fixed bed, thereby converting at least a portion of the feed;  
27
- 28 (j) fractionating the effluent of step (i) to produce gas, naphtha, and one or  
29 more middle distillate product streams, unconverted material being recycled  
30 to step (d).

## BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 illustrates a schematic flow diagram of the instant invention. It is a schematic of a two-stage hydrocracker. The second stage possesses at least two reaction zones.

Figure 2 illustrates the pilot plant simulations of two second-stage reaction zones in series.

## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

The instant invention is directed to a hydroprocessing method which is particularly useful in the second stage hydrocracking step of integrated processes such as those disclosed in U.S. Pat. No. 6,179,995 (09/227,235), an integrated process for hydroconverting a residuum feedstock.

Figure 1 illustrates a hydrocracking process in which there are at least two fixed bed reaction zones in series. Following each fixed bed reaction zone (prior to the last one in the series) is an intermediate flash zone for separation of converted materials from unconverted materials. In the fixed bed reaction zones, hydrogen is injected preferably in a co-current direction to the fixed bed effluent.

In Figure 1, the feedstock stream 1 enters the first hydroprocessing stage 3 (which comprises at least one fixed bed reactor), along with hydrogen stream 2. Streams 1 and 2 enter the top of the reactor and flow downward, contacting the fixed catalyst bed 4. The effluent 5 combines with product stream 25 to form stream 6. Stream 6 enters the fractionator 7, where it is separated into product streams, which are further discussed below. Product streams include gas 9, naphtha 10, kerosene 11, and diesel 12. The unconverted material, stream 13 boils above typically 700°F. It passes to the first reaction zone of stage 2, reactor 15. Stream 13 and 14 (the hydrogen stream) flow downward through

1 fixed hydrocracking catalyst bed 16. The effluent of reactor 15, stream 17  
2 passes to separation zone 18. Product, which boils below 700°F, is removed in  
3 stream 19. Stream 20, which contains unconverted material, enters the second  
4 reaction zone of stage 2, reactor 22, along with stream 21, which comprises  
5 hydrogen. Streams 20 and 21 flow downwardly through fixed hydrocracking  
6 catalyst bed 23. Stream 24, the effluent of reactor 22, combines with stream 19  
7 to form stream 25.

8  
9 The per-pass conversions in both reactors 15 and 22 are typically between 30%  
10 and 40%.

### 11 12 Feeds

13  
14 A wide variety of hydrocarbon feeds may be used in the instant invention.  
15 Typical feedstocks include any heavy or synthetic oil fraction or process stream  
16 having a boiling point above 392°F (200°C). Such feedstocks include vacuum  
17 gas oils, demetallized oils, deasphalted oil, Fischer-Tropsch streams, FCC and  
18 coker distillate streams, heavy crude fractions, etc. Typical feedstocks contain  
19 from 100-5000 ppm nitrogen and from 0.2-5 wt. % sulfur.

### 20 21 Products

22  
23 The hydrocracking process of this invention is especially useful in the production  
24 of middle distillate fractions boiling in the range of about 250-700°F (121-371°C).  
25 A middle distillate fraction is defined as having a boiling range from about 250 to  
26 700°F. The term "middle distillate" includes the diesel, jet fuel and kerosene  
27 boiling range fractions. The kerosene or jet fuel boiling point range refers to the  
28 range between 280 and 525°F (138-274°C). The term "diesel boiling range" refers  
29 to hydrocarbons boiling in the range from 250 to 700°F (121-371°C). Gasoline or  
30 naphtha normally boils in the range below 400° (204°C). Boiling ranges of

various product fractions recovered in any particular refinery will vary with such factors as the characteristics of the crude oil source, local refinery markets and product prices.

### Conditions

Hydroprocessing conditions is a general term which refers primarily in this application to hydrocracking or hydrotreating, preferably hydrocracking.

Hydrotreating conditions include a reaction temperature between 400°F-900°F (204°C-482°C), preferably 650°F-850°F (343°C-454°C); a pressure between 500 to 5000 psig (pounds per square inch gauge) (3.5-34.6 MPa), preferably 1000 to 3000 psig (7.0-20.8 MPa); a feed rate (LHSV) of 0.5 hr<sup>-1</sup> to 20 hr<sup>-1</sup> (v/v); and overall hydrogen consumption 300 to 2000 scf per barrel of liquid hydrocarbon feed (53.4-356 m<sup>3</sup>/m<sup>3</sup> feed).

Typical hydrocracking conditions include a reaction temperature of from 400°F-950°F (204°C-510°C), preferably 650°F-850°F (343°C-454°C). Reaction pressure ranges from 500 to 5000 psig (3.5-34.5 MPa), preferably 1500-3500 psig (10.4-24.2 MPa). LHSV ranges from 0.1 to 15 hr<sup>-1</sup> (v/v), preferably 0.25-2.5 hr<sup>-1</sup>. Hydrogen consumption ranges from 500 to 2500 scf per barrel of liquid hydrocarbon feed (89.1-445 m<sup>3</sup> H<sub>2</sub>/m<sup>3</sup> feed).

### Catalyst

A hydroprocessing zone may contain only one catalyst, or several catalysts in combination.

The hydrocracking catalyst generally comprises a cracking component, a hydrogenation component and a binder. Such catalysts are well known in the art. The cracking component may include an amorphous silica/alumina phase

1 and/or a zeolite, such as a Y-type or USY zeolite. Catalysts having high cracking  
2 activity often employ REX, REY and USY zeolites. The binder is generally silica  
3 or alumina. The hydrogenation component will be a Group VI, Group VII, or  
4 Group VIII metal or oxides or sulfides thereof, preferably one or more of  
5 molybdenum, tungsten, cobalt, or nickel, or the sulfides or oxides thereof. If  
6 present in the catalyst, these hydrogenation components generally make up from  
7 about 5% to about 40% by weight of the catalyst. Alternatively, noble metals,  
8 especially platinum and/or palladium, may be present as the hydrogenation  
9 component, either alone or in combination with the base metal hydrogenation  
10 components molybdenum, tungsten, cobalt, or nickel. If present, the platinum  
11 group metals will generally make up from about 0.1% to about 2% by weight of  
12 the catalyst. If noble metals are employed, poisoning is avoided due to the use  
13 of small reactors and the constant influx of hydrogen.

14  
15 Hydrotreating catalyst, if used, will typically be a composite of a Group VI metal  
16 or compound thereof, and a Group VIII metal or compound thereof supported on  
17 a porous refractory base such as alumina. Examples of hydrotreating catalysts  
18 are alumina supported cobalt-molybdenum, nickel sulfide, nickel-tungsten,  
19 cobalt-tungsten and nickel-molybdenum. Typically, such hydrotreating catalysts  
20 are presulfided.

## 21 22 EXAMPLES

23  
24 Figure 1 is a schematic of this invention. The effluent of a first-stage  
25 hydroprocessor passes to a fractionator. The unconverted portion of the first  
26 stage hydroprocessor passes to a second-stage hydrocracker. The  
27 second-stage hydrocracker comprises multiple reaction zones which are  
28 connected in series, with interstage separation zones. Unconverted material  
29 removed from each separation zone is passed to the next reaction zone and  
30 product is fractionated into middle distillate products and a recycle stream.



Figure 2 represents a pilot plant simulation of this invention. The feed to the second-stage hydrocracker is a hydrotreated Middle East vacuum gas oil. Fresh feed (represented by 100 units) joins with recycle (represented as 67 units) and passes to reaction zone 1. 40% per-pass conversion ( $67/167$ ) occurs, and products are removed by fractionation. Bottoms (33 units) are passed to reaction zone 1, where it is combined with recycle from reaction zone 2 (67 units) prior to entry into the reaction zone. 33% ( $33/100$ ) of the material is converted and fractionated as products. Per-pass conversion = fresh feed converted in a stage/total feed to a stage.

The Table below presents the conditions employed in this example. The recycle cut point is 700°F. The hydrogen partial pressure is 2100 psia. Three different scenarios are depicted. In the first case, a standard second-stage hydrocracking mode is employed, rather than the mode of this invention. The liquid hourly space velocity (LHSV) is  $1 \text{ hr}^{-1}$ . The per-pass conversion is 60%. The catalyst employed is an amorphous, base metal catalyst. In the second case, a zeolite loaded with noble metal is employed as the catalyst and the LHSV is  $2 \text{ hr}^{-1}$ . A standard second-stage mode is also employed, with 60% per-pass conversion.

The third case depicts a second-stage hydrocracker with more than one reaction zone, as in the instant invention. The same noble metal/zeolite catalyst as in the second case is employed. In the third case, the individual per-pass conversions for each reaction zone are 40% and 33%, respectively, while the overall per-pass conversion is 60%. The LHSV is  $2 \text{ hr}^{-1}$ .

As the Table below illustrates, second-stage distillate yield is greatest when the third case is employed.

<b><u>COMPARISON OF SECOND-STAGE ISOCRACKING YIELDS</u></b>			
<b>HDT Middle East VGO, 700°F Recycle Cut Point, ~2100 psia H<sub>2</sub></b>			
Case	1	2	3
Catalyst	Amorphous Base Metal	NMZ (Noble metal zeolite)	NMZ (Noble metal zeolite)
Conditions			
LHSV, 1/hr	1.0	2.0	2.0
PPC, %	60	60	40*
Mode	Standard	Standard	Two-stages with intermediate separation
Yields			
C <sub>4</sub> -	4.4	3.4	2.5
C <sub>5</sub> -250°F, LV%	22.6	22.0	16.4
250-550°F	51.3	60.3	56.4
550°F-700°F	34.0	26.9	35.1
250-700°F	85.3	87.2	91.5

1

2 \*Recycle liquid rate of 60% PPC.